POLYMERS FROM DIOLEFINS AND DIMERCAPTANS

BY

PAUL HARWOOD ALDRICH

B.A., University of Minnesota, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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IN THE GRADUATE COLLEGE OF THE
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Introduction

The use of the reaction between the sulfhydryl group and the carbon-carbon double bond to produce a polymer is not new.[1] However, at the time the work on this thesis was started, the molecular weights of the polymers produced from this reaction were of the order of 10,000 to 14,000, and this range in molecular weight was too low to make comparisons of these polymers with other high polymers of greatest interest. Thus, the primary purpose of this work has been to obtain higher molecular weight polymers from the reaction of the sulfhydryl group and the carbon-carbon double bond.

There are two common methods of obtaining higher molecular weight in polymers. First, a polymer with a low average molecular weight can be fractionated to obtain a fraction with a high average molecular weight. Second, means of obtaining a high molecular weight polymer directly in the polymerization reaction can be investigated.

A second purpose of this research has been to investigate the oxidation of the sulfide links in the polymers produced. It was felt that this might be a useful method of raising the melting points of the products since sulfones generally have higher melting points than the sulfides from which they are produced.

Discussion

Very little work has been done to determine the absolute molecular weights of the polymers prepared in this work. Comparisons of the molecular weights of the products were made by means of their intrinsic viscosity.

A considerable amount of work has been done on the polymerization of hexamethylenedithiol with biallyl. The first polymerizations attempted were repititions of the work

of Marvel and Chambers.[1] Their polymerizations were run in cyclohexane and initiated by irradiation with ultraviolet light. In the work for this thesis several modifications of their procedure were made, however. First, precautions were taken to guarantee the purity of the monomers. Second, the cyclohexane was carefully purified. Third, larger amounts of monomers were used in order to decrease the percentage error in weighing. Fourth, the air in the polymerization flask was replaced with nitrogen or carbon dioxide. However, even with these precautions the polymer obtained had about the same molecular weight as the best obtained by Marvel and Chambers.[1]

Fractionation of the polymers produced in these solution polymerizations was accomplished by dissolving in benzene and precipitation with methanol. From this operation it was possible to obtain a polymer with an intrinsic viscosity of more than 0.5. In the most favorable instances the fraction with this intrinsic viscosity represented 50 per cent of the theoretical yields for the polymerization. The highest intrinsic viscosity reported by Marvel and Chambers[1] was 0.29.

Emulsion polymerization using peroxide initiators with and without reduction activation has been the most successful means of obtaining higher molecular weights. Although the results have been erratic, the most promising system for the polymerization of hexamethylenedithiol with biallyl has been an initiator system consisting of ammonium persulfate, sodium metabisulfite and copper sulfate[2] used with MP 189-EF as the emulsifier. This system is rather sensitive to *p*H adjustments, and the *p*H range of 1.5-4.0 has given the best results. The highest molecular weight polymer obtained by the use of this system had an intrisic viscosity of 1.44. Usually the products have had an intrisic viscosity of 0.45-0.65. It has not been possible to determine the causes of the wide variation in the results with this system.

A proposed mechanism for the polymerization of hexamethylenedithiol with biallyl predicted that stopping the re-

action prematurely would result in a high yield of poylmer with a low molecular weight. Experimental evidence which agrees with this prediction has been obtained.

Investigation of the higher molecular weight polymers from hexamethylenedithiol and biallyl prepared either by fractionation of low molecular weight polymers or by emulsion polymerization has shown that orientable fibers could be drawn from a hot melt of the polymer. Orientation, which is obtained by stretching the freshly formed fiber, increased the length of the fiber to four times its original length. The unoriented fiber was opaque, and the oriented fiber was clear. It was found that it was possible to orient fibers from material with an intrinsic viscosity as low as 0.35. The fibers, however, were very weak unless the polymer used for the fiber had an intrinsic viscosity of 0.45 or more. That the stretched fibers were oriented was shown by X-ray patterns made of the stretched and unstretched fibers by Mr. R. S. Sprague.

Infrared absorption spectra of polymers which gave orientable fibers indicated that their structure was the same as the structure of the polymers obtained by Marvel and Chambers.[1] The infrared absorption spectra were determined by Mrs. E. M. Petersen.

Perbenzoic acid,[3,4] potassium permanganate[3,5] and ozone[6] have been used to oxidize the sulfide links in the polymer from hexamethylenedithiol and biallyl. Perbenzoic acid seems to give the most nearly complete oxidation of the polymer. Potassium permanganate and ozone degraded the polymer badly. Because no absolute molecular weights were determined it was not possible to determine whether perbenzoic acid caused degradation. Chambers' data on the use of perbenzoic acid[3] indicated that only half of the theoretical amount of perbenzoic acid was used in the oxidation of the polymer in spite of the fact that he obtained a high yield of oxidation product with an analysis which indicated that most of the sulfide links had been oxidized to sulfone links. The data obtained in this work indicated that 95 per cent of the theo-

retical amount of perbenzoic acid was required in the oxidation to obtain results which were similar to those of Chambers.

Allyl mercaptan and undecylenyl mercaptan have been prepared and polymerized, but neither have given a high molecular weight polymer. Undecylenyl mercaptan polymerized so readily that it was difficult to purify. Allyl mercaptan, which has been prepared by a new method, was difficult to polymerize. When it did polymerize, only liquid polymers was obtained.

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VITA

The author was born in Grand Rapids, Minnesota, on August 25, 1921. He attended the public schools of Minneapolis, Minnesota, and graduated from the Marshall High School in June, 1939. In September of that year he entered the University of Minnesota, from which he received the degree of Bachelor of Arts in August, 1942. He attended the graduate school of Iowa State College from September to December, 1942. During that time he was employed as a teaching assistant in the Chemistry Department of Iowa State College. From January, 1943, until June, 1946, he was employed as a chemist at the Minnesota Mining and Manufacturing Company in St. Paul, Minnesota. In September, 1946, he entered the graduate school of the University of Illinois. From that date until June, 1948, he was employed as a teaching assistant in the Chemistry Department of the University of Illinois. Since September, 1948, he held the Monsanto Chemical Company fellowship.

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